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Scope of Research

To understand the chemical structure and property in a molecular aggregated system, the keywords of molecular interactions and/or orientation are focused on, and the molecular aggregates are investigated by using originally developed spectroscopic techniques. The current major topics are: (1) Stratified Dipole-Arrays (SDA) theory accounting for bulk and molecular properties of perfluoroalkyl compounds; (2) the molecular orientation and conformation analysis in a thin film of an organic semiconductor; (3) the molecular structure and dynamics analysis of molecular water involved in a Nafion membrane.

KEYWORDS

Infrared and Raman Spectroscopy
Perfluoroalkyl Compounds
Polymer Electrolyte Membrane
Surface and Interface Chemistry
Organic Semiconductor



Selected Publications

Hasegawa, T.; Shimoaka, T.; Tanaka, Y.; Shioya, N.; Morita, K.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T., An Origin of Complicated Infrared Spectra of Perfluoroalkyl Compounds Involving a Normal Alkyl Group, *Chem. Lett.*, **44**, 834-836 (2015).
Hasegawa, T., Understanding of the Intrinsic Difference between Normal- and Perfluoro-alkyl Compounds toward Total Understanding of Material Properties, *Chem. Phys. Lett.*, **626**, 64-66 (2015).
Shioya, N.; Shimoaka, T.; Eda, K.; Hasegawa, T., A New Schematic of Poly(3-alkylthiophene) in an Amorphous Film Studied Using a Novel Structural Index on Infrared Spectroscopy, *Phys. Chem. Chem. Phys.*, **17**, 13472-13479 (2015).
Shimoaka, T.; Wakai, C.; Sakabe, T.; Yamazaki, S.; Hasegawa, T., Hydration Structure of the Strongly Bound Water on the Sulfonic Acid Group in a Nafion Membrane Studied by Infrared Spectroscopy and Quantum Chemical Calculation, *Phys. Chem. Chem. Phys.*, **17**, 8843-8849 (2015).
Wakai, C.; Shimoaka, T.; Hasegawa, T., ¹H NMR Analysis of Water Freezing in Nanospace Involved in a Nafion Membrane, *J. Phys. Chem. B*, **119**, 8048-8053 (2015).
Ishizuka, R.; Matubayashi, N.; Tu, K.-M.; Umebayashi, Y., Energetic Contributions from Cation and Anion to the Stability of Carbon Dioxide Dissolved in Imidazolium-Based Ionic Liquids, *J. Phys. Chem. B*, **119**, 1579-1587 (2015).

An Origin of Complicated Infrared Spectra of Perfluoroalkyl Compounds Involving a Normal Alkyl Group

Perfluoroalkyl (Rf) compounds containing a normal alkyl group often yield highly complicated infrared (IR) spectra especially in the CF stretching vibration (ν C-F) region. To reveal the reason behind this, the IR p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) is employed to measure a monolayer of $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_3\text{COOH}$ deposited on a silicon substrate. The compound is known to spontaneously aggregate to form a molecular assembly with the closest packing, in which the molecules are oriented perpendicular to the substrate. The IR pMAIRS spectra apparently prove that the complexity of the ν C-F region is due to the normal alkyl part directly connected to the Rf group because the carbons in the Rf group are vibrated as a coupled oscillator, and the oscillation of the alkyl part propagates to the Rf part along the molecular axis.

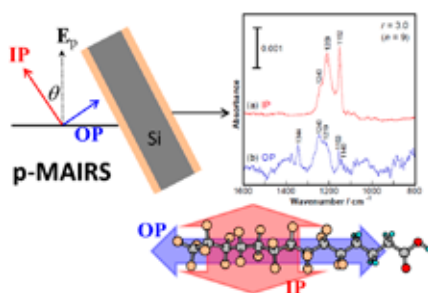


Figure 1. Schematic image of the CF stretching vibration mode. The complicated band is induced by the vibration along the molecular axis.

A New Schematic for Poly(3-alkylthiophene) in an Amorphous Film Studied Using a Novel Structural Index in Infrared Spectroscopy

The molecular structure of poly(3-alkylthiophene-2,5-diyl) in an amorphous film reveals that the short axis of the thiophene ring is kept highly oriented parallel to the substrate, whereas the long axis along the polymer chain is largely disordered. This is unveiled by infrared p-polarized multiple-angle incidence resolution spectroscopy (pMAIRS), achieved by analyzing the orientation angles of three mutually orthogonal vibrational modes localized on the thiophene ring with the aid of a newly developed structural index. This new analytical technique is useful irrespective of the crystallinity of the thin film. As a result, the intrinsic chemical parameters controlling the molecular orientation are understood in a unified manner, and the reason that the hexyl group gives the best results for a photovoltaic cell is also revealed.

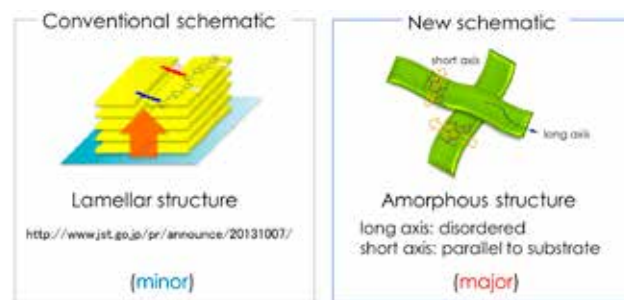


Figure 2. A new schematic of the face-on orientation in a thin film of poly(3-alkylthiophene).

Hydration Structure of Strongly Bound Water on the Sulfonic Acid Group in a Nafion Membrane Studied by Infrared Spectroscopy and Quantum Chemical Calculation

The hydration structure of the ‘strongly bound water’ around the sulfonic acid (SA) groups in Nafion, which has recently been revealed by ^1H NMR spectroscopy (*Anal. Chem.*, **85**, 7581 (2013)), is studied using infrared spectroscopy with the aid of quantum chemical (QC) calculations. During a heated drying process, bulky water is firstly dehydrated, which is followed by the disappearance of the hydronium ion and the appearance of bands that have been assigned to the fully dehydrated species at 140 °C. However, a spectral simulation based on QC reveals that the spectrum at 140 °C comes from the SA group associated with a single-water molecule via two H-bonds. This implies that a thoroughly dried membrane is unavailable even at 140 °C, and the involved water corresponds to the ‘strongly bound water.’ The QC-analytical results are experimentally confirmed by evolved gas analysis mass spectrometry (EGA-MS). At ca. 300 °C, which is the temperature where the SA group is selectively decomposed, the molecular fragment of SO_2 is observed accompanying water molecules as expected. This confirms that the last single-water molecule can remain on the SA group until the thermal decomposition.

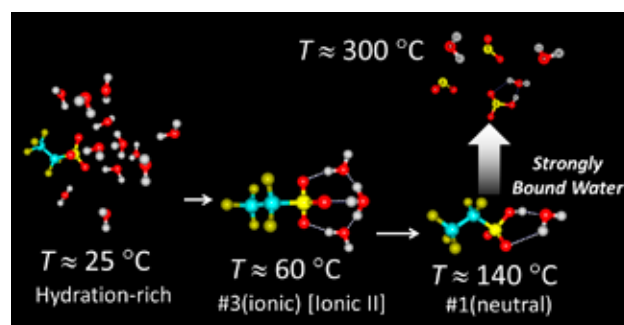


Figure 3. Dehydration and deionization process about sulfonic acid group in a Nafion membrane on heating.